

## Elastic constants of sodium from molecular dynamics

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We have performed molecular-dynamics calculations of the adiabatic elastic constants of sodium at three different temperatures,  $T=198$ , 299, and 349 K. Our method uses fluctuation formulas appropriate for the microcanonical ensemble which contain the elastic constants. In the simulation we have used a first-principles potential to model the interaction between the sodium atoms. The results, including the shear modulus  $C_{44}$ , show good agreement with experiment at all three temperatures. We have analyzed the contributions to the elastic constants from different types of terms appearing in the fluctuation formula and compared these contributions to other model-potential calculations. The volume dependence in the potential has considerable effect on the values of elastic constants. In comparison to some earlier calculations which employed pair potentials with no volume dependence, the fluctuation contributions to elastic constants  $C_{11}$  and  $C_{44}$  are noticeably large (20% of the value of the elastic constants in some cases). We find that the elastic constants do not change by much for the different potential-cutoff ranges employed: 17.85, 23.27, and 27.70 bohrs.

### I. INTRODUCTION

The molecular-dynamics method together with proper ensemble fluctuation formulas<sup>1</sup> has proven useful for calculating the adiabatic elastic constants for a Lennard-Jones system<sup>2</sup> and for silicon.<sup>3</sup> In these systems, the model potentials used depend only on the spatial positions of the particles. It has long been known that the interaction potentials and thus the properties of metals depend strongly on the density. For a realistic and consistent calculation of the elastic constants of metallic systems, the fluctuation method should be extended to include volume-dependent model potentials. In order to achieve this goal, one should obtain the proper microcanonical fluctuation formulas for elastic constants in the case of volume-dependent potentials.

The primary objective of this paper is to calculate the adiabatic elastic constants of metallic sodium from molecular dynamics. In this study we have used a model potential developed by Price and co-workers.<sup>4-6</sup> We briefly describe this model potential in Sec. II. Earlier theoretical studies of elastic constants of sodium include the lattice dynamics calculation by Glyde and Taylor<sup>7</sup> and Monte Carlo calculations by Cohen *et al.*<sup>8</sup> Both of these studies differ from the present calculation. The Monte Carlo calculation in Ref. 8 neglected the volume dependence of the pair potential which was pointed out also by Schiferl and Wallace.<sup>9</sup> Schiferl and Wallace<sup>9</sup> presented a molecular-dynamics calculation of the elastic constants of sodium using a potential developed by Wallace.<sup>10</sup> In their calculations, Schiferl and Wallace used canonical ensemble fluctuation formulas and added necessary correction terms in the spirit of Lebowitz, Percus, and Verlet<sup>11</sup> to obtain the adiabatic elastic constants. Schiferl and Wallace take the full volume dependence of the potential into account, and their method of calculation is therefore equivalent to our calculational method. In contrast to Ref. 9, we give and use the full

microcanonical fluctuation formulas to obtain the adiabatic elastic constants of sodium directly. In Sec. III we present the microcanonical molecular-dynamics method and give the statistical fluctuation formulas for the adiabatic elastic constants. In Sec. IV we describe the method of calculation and present the detailed results of the calculations. Finally, in Sec. V we discuss the results.

### II. MODEL POTENTIAL

The model potential employed in this study was described in detail in Refs. 4-6, and has the following form:

$$U(r, r_s) = \phi(r, r_s) + U_{\text{EG}}(r_s) + U_{\text{BS}}(r_s) + U_H(r_s), \quad (2.1)$$

where  $r_s$  is the density parameter defined as  $r_s = (3V/4\pi Z)^{1/3}$  and  $Z$  is the valence. The first term in Eq. (2.1) represents the pairwise interaction potential and has a long-range oscillatory behavior. The last three terms depend only on the volume; the electron-gas contribution is given by

$$U_{\text{EG}} = 0.982/r_s^2 + (0.407/\xi - 0.916)/r_s - (0.115 - 0.031 \ln r_s), \quad (2.2)$$

where  $\xi$  is related to the compressibility of the electron gas. The self-energy of the band structure is given by

$$U_{\text{BS}} = \phi(r=0, r_s). \quad (2.3)$$

The Hartree term represents the average interaction between the conduction electrons and the nonelectrostatic part of the bare potential; this term is adjusted so as to bring the lattice constant into agreement with the observed value at 0 K and is given by

$$U_H = 3ar_c^2/r_s^3. \quad (2.4)$$

By choosing  $a=0.218$ , not only the lattice parameter, but also the cohesive energy and the compressibility are brought into agreement with their respective values at 0 K. The quantity  $r_c$  in Eq. (2.4) is the core radius for the pseudopotential which has the value 1.694 bohrs.

### III. ELASTIC CONSTANTS IN MICROCANONICAL MOLECULAR DYNAMICS

In Ref. 1, Ray and Rahman, in addition to discussing constant tension  $HtN$  ( $H$  is the enthalpy and  $t$  the thermodynamic tension) molecular-dynamics methods, also presented the constant size and shape  $EhN$  form of molecular dynamics.  $E$  is the energy of the system,  $h$  is a  $3 \times 3$  matrix formed from the vectors  $\mathbf{a}$ ,  $\mathbf{b}$ , and  $\mathbf{c}$  which span the molecular-dynamics cell, and  $N$  is the number of particles in the cell. In the same paper, using the adiabatic differentiation method of Ray and Graben,<sup>12</sup> they

$$V_0 h_{0im}^{-1} h_{0jn}^{-1} h_{0kp}^{-1} h_{0lq}^{-1} C_{mnpq}^s = -4(\langle M_{ij} M_{kl} \rangle - \langle M_{ij} \rangle \langle M_{kl} \rangle) / k_B T + 2Nk_B T (G_{ik}^{-1} G_{lj}^{-1} + G_{il}^{-1} G_{kj}^{-1}) + \Psi_{ijkl} + \langle \Phi_{ijkl} \rangle, \quad (3.3)$$

where the angular brackets mean the time average of the term over the molecular-dynamics trajectory. The first term,  $-4(\langle M_{ij} M_{kl} \rangle - \langle M_{ij} \rangle \langle M_{kl} \rangle) / k_B T$ , we refer to as the fluctuation term; we shall call the second term  $2Nk_B T (G_{ik}^{-1} G_{lj}^{-1} + G_{il}^{-1} G_{kj}^{-1})$  the kinetic-energy term and the remaining terms:  $\Psi_{ijkl}$  the pure volume-dependent potential term and  $\Phi_{ijkl}$  the pair potential term. These four terms together give the elastic constants through Eq. (3.3). The quantity  $h_0$  is the value of  $h$  matrix at zero stress,  $V_0 = \det h_0$  and  $G_{ij}$  is the metric tensor  $G = \tilde{h}h$  where the tilde denotes matrix transposition. The matrix  $M_{ij} = \partial \mathcal{H} / \partial G_{ij}$  is related to the microscopic stress tensor  $\mathcal{P}_{ij}$  by

$$M = -Vh^{-1} \mathcal{P} \tilde{h}^{-1} / 2, \quad (3.4)$$

where  $\mathcal{P}_{ij}$  is defined by

$$V\mathcal{P}_{ij} = \sum_a p_{ai} p_{aj} / m_a - \sum_{a < b} \phi' x_{abi} x_{abj} / r_{ab}^2 - \left[ \sum_{a < b} \phi^* + \Psi^* \right] \delta_{ij}, \quad (3.5)$$

and the prime indicates  $r \partial / \partial r$  while the asterisk stands for  $V \partial / \partial V$ . The relation between strain tensor  $\epsilon$  and metric tensor  $G$  is

$$\epsilon = (\tilde{h}_0^{-1} G h_0 - 1) / 2. \quad (3.6)$$

also calculated the statistical fluctuation formulas for adiabatic elastic constants. Using the same method, we have derived the fluctuation formulas for a general volume-dependent potential which has the form

$$U(r_1, r_2, \dots, r_N; V) = \Phi(r_{12}, r_{13}, \dots, V) + \Psi(V), \quad (3.1)$$

where the first term,

$$\Phi(r_{12}, r_{13}, \dots, V) = \sum_{a < b} \phi(r_{ab}, V), \quad (3.2)$$

is the total effective pair potential and  $\Psi$  is the strictly volume-dependent potential.

Since the method of derivation is by now standard, we shall present the result. The fluctuation formulas for the elastic constant have the form

The explicit form of strictly volume-dependent term  $\Psi_{ijkl}$  is

$$\Psi_{ijkl} = 4\partial^2 \Psi / \partial G_{ij} \partial G_{kl} = \Psi^{**} G_{ij}^{-1} G_{kl}^{-1} - \Psi^* (G_{ik}^{-1} G_{lj}^{-1} + G_{il}^{-1} G_{kj}^{-1}), \quad (3.7)$$

while the pair potential term  $\Phi_{ijkl}$  is

$$\begin{aligned} \Phi_{ijkl} &= 4\partial^2 \Phi / \partial G_{ij} \partial G_{kl} \\ &= \sum_{a < b} (\phi'' - 2\phi') (s_{abi} s_{abj} s_{abk} s_{abl} / r_{ab}^4) \\ &\quad + \sum_{a < b} \phi'^* (s_{abi} s_{abj} G_{kl}^{-1} + G_{ij}^{-1} s_{abk} s_{abl}) / r_{ab}^2 \\ &\quad + \sum_{a < b} \phi^{**} G_{ij}^{-1} G_{kl}^{-1} - \sum_{a < b} \phi^* (G_{ik}^{-1} G_{lj}^{-1} + G_{il}^{-1} G_{kj}^{-1}), \end{aligned} \quad (3.8)$$

and  $s_{abi} = s_{ai} - s_{bi}$  is the scaled coordinate difference between particles  $a$  and  $b$ .

Recently, Pearson *et al.*,<sup>13</sup> using Laplace transform techniques, derived exact formulas containing the elastic constants in the microcanonical ensemble. In the thermodynamical limit the formulas obtained by this method are equivalent to the ones obtained through the adiabatic differentiation method.<sup>14</sup> For completeness, we present the exact fluctuation formulas for the elastic constants obtained by using the Laplace transform method

$$\begin{aligned} V_0 h_{0im}^{-1} h_{0jn}^{-1} h_{0kp}^{-1} h_{0lq}^{-1} C_{mnpq}^s &= \Psi_{ijkl} + \langle \Phi_{ijkl} \rangle + Nk_B T [(G_{ik}^{-1} G_{lj}^{-1} + G_{il}^{-1} G_{kj}^{-1}) + G_{ij}^{-1} \gamma_{kl} + G_{kl}^{-1} \gamma_{ij} - G_{ij}^{-1} G_{kl}^{-1} Nk_B / C_\epsilon] \\ &\quad - (3N/2 - 1) [\langle (\Phi_{ij})(\Phi_{kl}) K^{-1} \rangle - \langle (\Phi_{ij}) K^{-1} \rangle \langle \Phi_{kl} \rangle \\ &\quad - \langle \Phi_{ij} \rangle \langle (\Phi_{kl}) K^{-1} \rangle + \langle \Phi_{ij} \rangle \langle \Phi_{kl} \rangle \langle K^{-1} \rangle], \end{aligned} \quad (3.9)$$

where

$$\Phi_{ij} = 2\partial\Phi/\partial G_{ij} ,$$

or explicitly

$$\Phi_{ij} = \sum_{a,b} \phi' s_{abi} s_{abj} / r_{ab}^2 + \sum_{a,b} \phi^* G_{ij}^{-1} . \quad (3.10)$$

$C_\epsilon$  is the constant-strain specific heat determined from

$$k_B/C_\epsilon = 1 - (1 - \frac{2}{3}N) \langle K \rangle \langle K^{-1} \rangle , \quad (3.11)$$

and the "Grüneisen tensor,"  $\gamma_{ij} = V(\partial t_{ij}/\partial E)_\epsilon$ , is determined by the exact formula

$$\begin{aligned} h_{0ki}^{-1} h_{0lj}^{-1} \gamma_{ij} &= G_{kl}^{-1} N k_B / C_\epsilon \\ &+ (3N/2 - 1) \\ &\times [\langle \Phi_{kl} \rangle \langle K^{-1} \rangle - \langle (\Phi_{kl}) K^{-1} \rangle] . \end{aligned} \quad (3.12)$$

Equation (3.9) represents the exact fluctuation formula for the adiabatic elastic constants.

Equations (3.3) or (3.9) are very general in the sense that they can be used for anisotropic solids with any or no symmetry (including amorphous solids), and a general shape of the computational cell, and they are also applicable to systems under conditions of arbitrary strain. In our calculations we have mainly used Eq. (3.3). We have also tested the differences between the exact formula Eq. (3.9) and the thermodynamical limit formula Eq. (3.3) for one temperature. We shall discuss these results later. If the elastic constant calculation is performed for the zero-strain state, i.e.,  $h = h_0$ , then Eq. (3.3) reduces to the following form:

$$\begin{aligned} V_0 C_{ijkl}^s &= -(\langle \mathcal{P}_{ij} \mathcal{P}_{kl} \rangle - \langle \mathcal{P}_{ij} \rangle \langle \mathcal{P}_{kl} \rangle) V_0^2 / k_B T + 2N k_B T (\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}) \\ &+ \Psi^{**} \delta_{ij} \delta_{kl} - \Psi^* (\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}) + \left\langle \sum_{a < b} (\phi'' - 2\phi') x_{abi} x_{abj} x_{abk} x_{abl} / r_{ab}^4 \right\rangle \\ &+ \left\langle \sum_{a < b} \phi^* (x_{abi} x_{abj} \delta_{kl} + \delta_{ij} x_{abk} x_{abl}) / r_{ab}^2 \right\rangle + \left\langle \sum_{a < b} \phi^* \delta_{ij} \delta_{kl} \right\rangle - \left\langle \sum_{a < b} \phi^* (\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}) \right\rangle , \end{aligned} \quad (3.3')$$

which is obtained through multiplying both sides of Eq. (3.3) by four  $h_0$ 's and setting  $G = G_0$ . The zero-strain form of Eq. (3.9) could also be obtained in a similar way.

#### IV. MOLECULAR-DYNAMICS RESULTS

##### A. Method of calculation

As previously mentioned, we performed calculations at three different temperatures:  $T = 197.9$ ,  $298.8$ , and  $348.6$  K, for a system of 432 sodium atoms arranged in a bcc lattice. The potential was truncated at a distance  $R_c = 23.27$  bohrs. With this cutoff range, the average number of atoms interacting with each atom is 180, i.e., the first 11 neighbor shells of the bcc lattice are included.

To determine  $h_0$ , we performed simulations with variable size and shape  $HtN$  molecular dynamics with the tension (or stress) equal to zero. At the end of these runs (20 000 time steps with each time step being  $6.85 \times 10^{-16}$  s) the average value of  $h$ , i.e.,  $h_0$ , was obtained. However, the calculated value of  $h_0$  in these runs gave rise to densities lower than the experimental densities for sodium. For instance, the difference between the calculated density and experimental zero-pressure density is 2.3% at 299 K. This density discrepancy at high temperatures was previously noticed in the liquid-state studies.<sup>6</sup> Eventually, we decided to perform calculations at the zero-pressure experimental density. This was arranged by adding a correction term to the potential, namely  $P_{\text{ext}} V$ , which is a positive external pressure applied to bring the system to the desired density. Thus, we correct the potential in order to obtain the experimental density. The size of the molecular-dynamics cell, in other words, the density at each temperature, is determined from thermal expansion data for sodium by Aldhart *et al.*<sup>15</sup> and Seigel and Quim-

by.<sup>16</sup>

Next we constructed a perfect bcc lattice within a cubic molecular-dynamics cell, and the system was brought to the proper temperature by scaling the velocities. Before starting the elastic constant calculation preliminary molecular dynamics runs of 6–8 ps (of the order of 10 000 time steps) were performed to equilibrate the system at the temperatures  $T = 197.9$ ,  $298.8$ , and  $348.6$  K.

Due to the cubic symmetry of the bcc crystal, there are only three independent nonzero elastic constants which, in Voigt notation, are

$$\begin{aligned} C_{11} &= C_{22} = C_{33} , \\ C_{12} &= C_{23} = C_{31} , \\ C_{44} &= C_{55} = C_{66} . \end{aligned} \quad (4.1)$$

Using Eq. (3.3), we calculated these nine elastic constants independently. Also, for a check of the calculation we calculated  $C_{43}$ , which should be, and was to the accuracy of our calculation, zero. Calculating all nine elastic constants allows one to follow the convergence of the calculation by comparing terms that should be equal by cubic symmetry, e.g.,  $C_{11}$ ,  $C_{22}$ ,  $C_{33}$ . At the end of the calculation, we used these independently determined values to calculate symmetry-averaged elastic constants and give an estimate of error for each independent component.

##### B. Results

We present the results of our calculations of elastic constants at  $T = 197.9$ ,  $298.8$ , and  $348.8$  K with 432 atoms together with experimental values in Table I. In these calculations, the cutoff distance for the interaction potential is taken to be 23.27 bohrs. In the table contributions from the pair-potential term, pure volume-dependent potential term, kinetic-energy term, and fluc-

tuation term are tabulated separately. These quantities were calculated using molecular-dynamics runs of 12 000 time steps (8.22 ps). Densities corresponding to these temperatures are  $\rho = 0.989, 0.970$ , and  $0.960 \text{ g/cm}^3$ , respectively. The experimental values are gathered from measurements of Diederich and Trivosonno,<sup>17</sup> Daniels,<sup>18</sup> Martinson,<sup>19</sup> and Fritsch *et al.*<sup>20</sup>

The calculated values without pressure corrections are observed to be lower than experiment by 3–10 % with the largest percentage differences occurring for  $C_{12}$ . As described earlier, performing calculations at the experimental density implies a modification in the potential. Taking into account the effect of the correction term added to the potential, we have the following pressure corrections to the elastic constants:

$$C_{11} \rightarrow C_{11} - P, \quad C_{12} \rightarrow C_{12} + P, \quad C_{44} \rightarrow C_{44} - P, \quad (4.2)$$

where  $P$  is the added pressure. For these runs, the pressure corrections are found to be 1.09, 1.36, and 1.58 kbar

at 197.9, 298.8, and 348.6 K, respectively. Even though the pressure corrections are small (1.4–2.3 % for  $C_{11}$ , 1.8–2.8 % for  $C_{12}$ , and 2.2–4.2 % for  $C_{44}$ ) they are not negligible. The percentage differences between the calculated elastic constants with the pressure corrections and experimental values are 4–8 % for all three moduli at each temperatures. Note also that the results show a softening with increasing temperatures very similar to the experimental values. Especially the softening in the shear modulus is noticeable as the temperature is elevated.

The major contribution to all elastic constants comes from the pair potential. Pure volume-dependent potential contributions are negative for  $C_{11}$  and  $C_{44}$  and positive for  $C_{12}$ , but all are of the same order of magnitude, namely 10 kbar. Fluctuation contributions are large and negative for  $C_{11}$  and  $C_{44}$ , and positive and small for  $C_{12}$ . Fluctuation contributions increase as the temperature increases, implying a broader distribution of the microscopic stress tensor.

TABLE I. Contributions to adiabatic elastic constants from different terms in Eq. (3.3) and experimental values of elastic constants at  $T = 199, 299$ , and  $349 \text{ K}$ . The cutoff range in these calculations is 23.27 bohrs. All entries are in kbar. The calculations were for 12 000 time steps.

	$C_{11}$	$C_{12}$	$C_{44}$
$T = 197.9 \text{ K}$			
Pair-potential term	90.38	45.62	63.60
Strictly volume-dependent term	−9.22	11.38	−10.30
Kinetic-energy term	2.83	0.00	1.42
Fluctuation term	−9.01	2.84	−5.79
Subtotal	74.98	59.84	48.93
Pressure correction	−1.09	1.09	−1.09
Total theory	$73.89 \pm 0.66$	$61.93 \pm 0.48$	$47.84 \pm 0.83$
Experiment	$76.5,^a 81.2^c$	$63.9,^a 67.9^c$	$50.0,^a 50.9^c$
$T = 298.8 \text{ K}$			
Pair-potential term	89.83	42.51	58.29
Strictly volume-dependent part term	−9.63	11.06	−10.34
Kinetic-energy term	4.19	0.00	2.09
Fluctuation term	−10.73	3.12	−8.56
Subtotal	73.66	56.69	41.48
Pressure correction	−1.36	1.36	−1.36
Total theory	$72.30 \pm 2.27$	$58.05 \pm 1.52$	$40.12 \pm 0.59$
Experiment	$73.8,^b 76.9^c$	$62.1,^b 64.7^c$	$41.9,^b 43.4^c$
$T = 348.6 \text{ K}$			
Pair-potential term	90.83	40.70	55.50
Strictly volume-dependent part term	−9.82	11.91	−10.37
Kinetic-energy term	4.83	0.00	2.42
Fluctuation term	−13.81	3.71	−10.36
Subtotal	72.04	55.32	37.19
Pressure correction	−1.58	1.58	−1.58
Total theory	$70.46 \pm 1.68$	$56.90 \pm 1.80$	$35.61 \pm 0.57$
Experiment	$74.3^d$	$60.6^d$	$39.6^d$

<sup>a</sup>Reference 17.

<sup>b</sup>Reference 18.

<sup>c</sup>Reference 19.

<sup>d</sup>Reference 20.

TABLE II. Calculated adiabatic elastic constants at 299 K for three different cutoff distances. The calculation with cutoff range 17.85 bohrs was run for 25 000 time steps while the other two calculations were run for 12 000 time steps. All entries are in kbar.

	$C_{11}$	$C_{12}$	$C_{44}$
$N=432$ , $R_c=17.85$ bohrs			
Pair-potential term	87.23	42.41	57.24
Strictly volume-dependent term	-9.63	11.06	-10.34
Kinetic-energy term	4.19	0.00	2.09
Fluctuation term	-11.02	3.24	-8.72
Total without pressure correction	70.77	56.71	40.27
$N=432$ , $R_c=23.27$ bohrs			
Pair-potential term	89.83	42.51	58.29
Strictly volume-dependent term	-9.63	11.06	-10.34
Kinetic-energy term	4.19	0.00	2.09
Fluctuation term	-10.73	3.12	-8.56
Total without pressure correction	73.66	56.69	41.48
$N=686$ , $R_c=27.70$ bohrs			
Pair-potential term	90.56	42.87	57.75
Strictly volume-dependent term	-9.63	11.06	-10.34
Kinetic-energy term	4.18	0.00	2.09
Fluctuation term	-14.11	4.26	-8.44
Total without pressure correction	71.00	58.19	41.05

### C. Range dependence

As pointed out in Sec. II, the model potential we are employing for sodium shows an oscillatory long-range behavior. In molecular-dynamics simulations using potentials with long-range behavior, a concern is the choice of a reasonable distance to truncate the potential. With this in mind, we have repeated the elastic constant calculation at 299 K for two additional cutoff distances,  $R_c=17.85$  bohrs and  $N=432$  atoms for 25 000 time steps and  $R_c=27.70$  bohrs and  $N=686$  atoms for 12 000 time steps. In Table II the results for these three ranges are given. As seen from Table II, the differences in the values of elastic constants at the different ranges are

small. These differences are caused by the changes in the pair-potential term and fluctuation term. When the cutoff distance is changed from 23.27 to 17.85 bohrs the decrease in the pair-potential contribution to  $C_{11}$ , 2.6 kbar, is significant in comparison to the accuracy of calculation. The changes in the pair-potential contributions for  $C_{12}$  and  $C_{44}$  are not as large as in  $C_{11}$  for these two calculations. This point is further clarified in Table III, where we present different type of terms which make up the pair-potential contribution to elastic constants. Even though the changes in the terms which make up pair-potential correction are large from one range to another, the sum remains almost the same. Comparing the re-

TABLE III. Contributions to the pair potential term at 299 K for three different cutoff distances. These are for the same three runs given in Table II. All entries are in kbar.

	$C_{11}$	$C_{12}$	$C_{44}$
$N=432$ , $R_c=17.85$			
$r$ derivatives	80.84	50.24	50.24
$V$ derivatives	5.06	-9.95	7.00
Mixed derivatives	2.33	2.33	0.00
Total pair-potential term	87.23	42.41	57.24
$N=432$ , $R_c=23.27$			
$r$ derivatives	84.65	51.30	51.30
$V$ derivatives	3.90	-10.06	6.99
Mixed derivatives	1.27	1.27	0.00
Total pair-potential term	89.82	42.51	58.29
$N=686$ , $R_c=27.70$			
$r$ derivatives	85.05	50.95	50.95
$V$ derivatives	2.32	-10.28	6.80
Mixed derivatives	2.19	2.19	0.00
Total pair-potential term	90.56	42.87	57.75

TABLE IV. Adiabatic elastic constants and different contributions to elastic constants at 299 K calculated for 25 000 time steps run with a cutoff range of 17.85 bohrs, using exact fluctuation formula for elastic constants, Eq. (3.9). All entries are in kbar.

	$C_{11}$	$C_{12}$	$C_{44}$
Potential term	87.23	42.41	57.24
Pure volume-dependent term	-9.63	11.06	-10.34
Kinetic-energy term	2.09	0.00	1.05
$\gamma$ -dependent term	2.62	2.62	0.00
$C_\epsilon$ -dependent term	-0.32	-0.32	0.00
Fluctuation term	-12.66	1.65	-8.74
Total	69.33	57.42	39.21

sults for the 23.27- and 27.70-bohr calculations term by term using Tables II and III, we observe the changes are small for almost all types of terms with the only exception being the change in the fluctuation term for  $C_{11}$ . Thus we feel that our elastic constant calculations performed by using a cutoff range of 23.27 bohrs give satisfactory results.

#### D. Comparison of exact and thermodynamical limit formulas

In order to compare Eqs. (3.3) and (3.9) we have used the data saved during the 25 000 time-step run with 432 atoms at 299 K with the cutoff range  $R_c = 17.85$  bohrs. We calculated  $C_\epsilon/Nk_B$  and  $\gamma_{ij}$  by using Eqs. (3.11) and (3.12), respectively. Due to cubic symmetry there is only one independent nonzero component for  $\gamma_{ij}$ , i.e.,  $\gamma_{ij} = \gamma\delta_{ij}$ , where  $\gamma$  is the Grüneisen parameter. We found  $C_\epsilon/Nk_B = 3.278$  [experimental value 3.264 (Ref. 21)] and the symmetry-averaged value for Grüneisen parameter  $\gamma = 1.251$  [experimental value  $\gamma = 1.27$  (Ref. 15)]. Using these values for  $C_\epsilon/Nk_B$  and  $\gamma$ , the elastic constants calculated from Eq. (3.9) and the different contributions are tabulated in Table IV. Comparing these results with the results obtained from the thermodynamical limit formula for the same run, Table II, we conclude that the differences are small in comparison to the accuracy of calculation for the system under consideration.

#### V. CONCLUDING REMARKS

The elastic constants calculated using Eq. (3.3) and the sodium potential constructed by Price *et al.* show good agreement with experimental data at  $T = 198, 299$ , and 349 K. The differences between calculated and experimental values are within 4–8 % for all the elastic constants.

An important feature of this calculation is the agreement of the calculated values of the shear modulus  $C_{44}$  with experimental values. In a previous molecular-dynamics calculation<sup>9</sup> the calculated values for  $C_{44}$  showed similar softening with increasing temperature, but the values compared to experiment were too small. For instance, from Ref. 9, the results for  $C_{44}$  were 41.7, 35.4, and 30.2 kbar at 199, 297, and 340 K, respectively. The differences between these calculated values and the

experimental values for  $C_{44}$  are considerably larger than the differences found in our calculation. Schiferl and Wallace suggest that this large discrepancy in  $C_{44}$  is due to the use of only second-order perturbation theory in the derivation of interaction potential. It is necessary to point out that the potential employed in our calculation is also obtained by using second-order perturbation theory. We also observed that the magnitudes of the pair potential and pure volume-dependent potential contributions to elastic constants in Ref. 9 are much larger than the ones obtained in this study. For example, the pair-potential contribution to  $C_{11}$  at 297 K is 121.11 kbar in Ref. 9, whereas it is only 89.83 kbar at 299 K in our calculation. As for the pure volume-dependent potential contributions to  $C_{11}$ , they are -9.63 kbar in our study and -38.92 kbar in Ref. 9. We feel that further study is necessary to clarify the large differences between the results obtained from these two potentials.

Other important characteristics of our calculation are the large contributions from fluctuation terms and the terms involving volume derivatives of pair potential. As an example at 349 K, the fluctuation contribution for  $C_{44}$  becomes almost 20% of the pair-potential term while for  $C_{11}$  it is 15%. The neglect of volume dependence of the pair potential in calculating elastic constants of sodium may introduce substantial error to the results as can easily be seen from Table III.

Our investigation of range dependence has shown that the calculation of the elastic constants is not very sensitive to the potential-cutoff ranges employed. We find essentially the same values for the elastic constants at the three ranges that were used.

Finally, the comparison of the exact Eq. (3.9) and thermodynamic limit Eq. (3.3) fluctuation formulas for elastic constants gave the same results within the accuracy of calculations.

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